

(19) 日本国特許庁 (J P)

(12) 特 許 公 報 (B 2)

(11) 特許番号

第2506594号

(45) 発行日 平成8年(1996)6月12日

(24) 登録日 平成8年(1996)4月2日

(51) Int. CL<sup>8</sup>

識別記号

片内整理番号

P I

技術表示箇所

C 0 9 B 67/48

C 0 9 B 67/48

A

請求項の数1(全 4 頁)

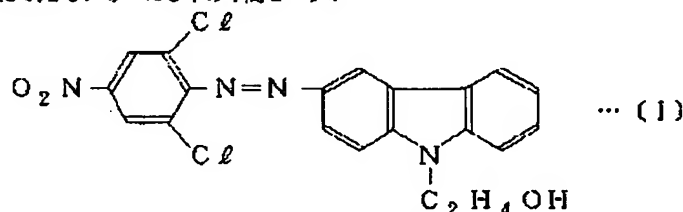
(21) 出願番号	特願平4-6844	(73) 特許権者	395017108 ダイスタージャパン株式会社 大阪府大阪市中央区安土町一丁目7番20号
(22) 出願日	平成4年(1992)1月17日	(72) 発明者	姫野 清 北九州市八幡西区黒崎城石1番1号 三菱化成ヘキスト株式会社研究所内
(65) 公開番号	特開平5-194874	(72) 発明者	松原 利夫 北九州市八幡西区黒崎城石1番1号 三菱化成ヘキスト株式会社研究所内
(43) 公開日	平成5年(1993)8月3日	(72) 発明者	渡野 美治 北九州市八幡西区黒崎城石1番1号 三菱化成ヘキスト株式会社研究所内
		審査官	田中 倫子

(54) 【発明の名称】 水不溶性モノアゾ染料

(57) 【特許請求の範囲】

【請求項1】 回折角(2θ)約11.3°、24.4°及び約27.0°に3本の強いピーク、更に約10.3°、21.1°及び約29.5°に3本の中間ピーク\*

\*を示すX線回折図(CuKα)により特徴づけられる結晶状態を有する下記構造式(1)



で示される水不溶性モノアゾ染料。

【発明の詳細な説明】

【0001】

\*を示すX線回折図(CuKα)により特徴づけられる結晶状態を有する下記構造式(1)

【化1】

【産業上の利用分野】 本発明はモノアゾ染料に関するもので、詳しくは、高温で苛酷な条件でもポリエステル繊維等を均一に染色することのできる新規な結晶状態を有

BEST AVAILABLE COPY

(2)

特許2506594

3

する黄色系モノアゾ染料に関するものである。

【0002】

【従来の技術】近年、染色業界では染色法に種々の合理化が行われており、例えば、分散染料を用いてポリエステル繊維を染色する場合に於ては、布用としては液流染色法、糸用としてはチース染色法又はパッケージ染色法等があり、広く行なわれている。

【0003】これらの染色法は、静止した繊維を何層にも巻いた緻密な層内に、染色分散液を強制的に循環させて染色させる方式であるため、従来以上に、染色浴に分散した染料粒子が微粒子であること及び染色浴における分散安定性が保れていることが要求される。もし、染料粒子が大きくなると、繊維層によって染料粒子の透過現象が起り、繊維内部への染料の浸透不良、あるいは凝集物の付着による内層または外層の濃淡染め、繊維表面のみへの染料の付着による耐摩擦堅牢度などの堅牢度の低下などの問題が発生する。

【0004】従って、このような染色法に使用する染料は、染色中で分散が良好であり、かつ室温から実際の染色が起る高温までの広い温度範囲において分散性が低下しないことが必要である。ところが、一般的に、染色浴中で高温にした時、染料の分散性は、往々にして低下しやすく、その結果、凝集した染料が上述したように被染物の表面に透過残渣状に付着し、また何層にも重なっている被染物は、外層部分と内層部分で染色濃度が異なり、均一な濃度の染色物が得られない。

【0005】特に最近、省資源、省エネルギーの観点から、①染色浴の低浴比化（被染物：染色液の比率を1：30から1：10に低下）、②分散剤の使用割合の低下（染料：分散剤の比率を1：3から1：1に低下）、更に、③染色条件の一層の短時間高温化（130℃で1時間から135℃で0.5時間）など、染色条件が苛酷な条件に移行しつつあるが、これらの条件はいずれも、染料の分散安定性には不利に働く為、従来の染色法では比較的分散安定性の良好であった染料においても、より厳しい最近の染色法においては、分散安定性が不良となるものも少なくない。

【0006】例えば、請求項1に記載の構造式〔I〕で示されるカルバゾール系のモノアゾ染料は、その構造自体は、ドイツ特許2212755により公知であり、その製法としては常法に従って、ジアゾ成分とカップリング成分とをカップリング反応させることにより得られる。このモノアゾ染料は従来の温和な染色条件においては、ポリエステル繊維を均一に染色することができ、しかも耐堅牢度も優れたものである。ところが上述のような高温で、苛酷な条件下で染色を行なった場合には、染料の分散性の低下が著しく、均一な染色濃度の染色物を得ることが極めて困難である。

【0007】また、この染料は各種染色助剤との相溶性の点でも問題があり、例えば、芒硝（Na<sub>2</sub>SO<sub>4</sub>）存

4

在下での高温分散安定性が著しく悪く、従って反応性染料等と併用してポリエステル/綿混紡品を芒硝の存在下で染色する際に不均染となる。更に、染料を配合し使用する際にも、配合染料との相溶性の点から色ブレ、不均染を発生する欠点があった。

【0008】

【発明が解決しようとする課題】本発明は上記欠点を解決した、高温で苛酷な条件下でも良好な染色を行うことができる染料を提供するものである。本発明者らは上記欠点に関して鋭意検討した結果、請求項1に記載の構造式〔I〕で示されるカルバゾール系のモノアゾ化合物には少なくとも2種類の結晶変態が存在すること、その1つは高温の染色条件下では分散安定性はあまり良好でない結晶変態であり、従来の通常の合成反応で得られるケーキは該結晶変態であること、他の1つは高温でしかも苛酷な染色条件下でも分散安定性が非常に良好である新規な結晶変態であることを見出した。さらに染料組成物の高温染色中での分散状態の安定性は、染料粒子の大小のみではなく、結晶変態に重大な関係があり、上記の新規な結晶変態の化合物を用いた場合に、初めて染料組成物の高温染色中での分散安定性が達成できることを見出し本発明に到達した。

【0009】

【課題を解決するための手段】即ち本発明の要旨は、回折角（2θ）約11.3°、24.4°及び約27.0°に3本の強いピーク、更に約10.3°、21.1°及び約29.5°に3本の中間ピークを示すX線回折図（CuKα）により特徴づけられる結晶変態を有する、請求項1に記載の構造式〔I〕で示される水不溶性モノアゾ染料を要旨とする。本発明の新規な結晶変態（以下、α型結晶変態と言う）を有するモノアゾ化合物は以下のようにして得ることができる。例えば、2,6-ジクロル-4-ニトロアニリンを常法によりジアゾ化し、次いで、これを希硫酸媒体中で-5～15℃、好ましくは0～10℃の温度で0.5～15時間、カップラーであるN-(ヒドロキシエチル)カルバゾールとカップリング反応させることにより、前記構造式〔I〕のモノアゾ化合物を合成する。この合成で得られるモノアゾ化合物のケーキはほぼ無定型に近い結晶変態（以下β型結晶変態と言う）であるが、本発明ではこのケーキを更に、特定条件下で処理することによりα型結晶変態とする。この処理方法としては、例えば、β型結晶変態のケーキを①水媒体中に分散し、場合により、ナフタレンスルホン酸のホルムアルデヒド縮合物、リグニンスルホン酸ソーダが主成分であるサルファイトパルプ廃液の濃縮物等の分散剤の存在下、60～130℃、好ましくは80～100℃の温度で0.5～30時間、好ましくは1～10時間、攪拌処理する方法、又は②メタノール、エタノール又はブタノールなどのアルコール類、ジオキサンなどのエーテル類、エチレングリコール、グリコールエー

(3)

特許2506594

5

テル等の有機溶媒中に分散し、15～100℃、好ましくは20～80℃の温度で0.5～10時間程度、攪拌処理する方法が採用される。

【0010】次に、前示構造式(1)で示されるモノアゾ化合物の $\alpha$ 型結晶変態と $\beta$ 型結晶変態について図面により説明する。図1及び図2は粉体X線回折法におけるCuK $\alpha$ 線による回折状態をプロポーショナルカウンタを使用して記録したX線回折図であり、横軸は回折角(2 $\theta$ )、縦軸は回折強度を示す。図1は本発明の新規な結晶型である $\alpha$ 型結晶変態を示すもので、特に、回折角(2 $\theta$ )約11.3°、24.4°及び約27.0°に3本の強いピーク、更に約10.3°、21.1°及び約29.5°に3本の中間ピークを持っている。図2は従来の $\beta$ 型結晶変態を示すものであり、図1の $\alpha$ 型結晶変態と明確に異なっている。

【0011】X線回折法による回折角は、同一結晶型のものであれば、 $\pm 0.1^\circ$ 程度の誤差で常に一致するものであって、これらの図面は結晶変態の相違を明白に示している。この結晶型の差異により染色時におけるモノアゾ化合物の挙動が異なり、本発明の場合には、高温度で、しかも、苛酷な条件での染色法を採用しても、良好な染色ができるのである。

【0012】本発明のカルバゾール系のモノアゾ染料により染色しうる繊維類としてはポリエチレンテレフタレート、テレフタル酸と1,4-ビス-(ヒドロキシメチル)シクロヘキサンの重縮合物などよりなるポリエステル繊維、あるいは木綿、羊毛などの天然繊維と上記ポリエステル繊維との混紡品、混織品が挙げられる。本発明のモノアゾ染料を用いてポリエステル繊維を染色するには、常法により分散剤としてナフタレンスルホン酸とホルムアルデヒドとの縮合物、高級アルコール硫酸エステル、高級アルキルベンゼンスルホン酸塩などを用いて、水性媒体中に分散させた染色浴または擦染液を調製し浸染又は擦染を行なうことができる。また、例えば、浸染の場合、上述のような高温染色法、キャリアー染色法、サーモゾル染色法などの染色処理法を適用することもでき、しかも、これらの方法で苛酷な染色条件を採用しても、本発明のモノアゾ染料は分散安定性に優れているので、ポリエステル繊維ないしはその混紡品を良好に染色することができる。具体的には、ポリエステル繊維類を染色温度125～140℃、染浴比が15倍以下、染料に対する分散剤の使用割合が3重量倍以下の苛酷な条件下で、水性媒体中、分散剤の存在下で吸着染色することも可能である。

【0013】尚、場合により染色浴にキ酸、酢酸、リン酸、硫酸アンモニウムなどの酸性物質を添加すれば、更に好結果が得られる。また、本発明方法に使用される前示構造式(1)で示されるモノアゾ染料は他の染料と併用してよく、染料相互の配合により染色性の向上等好結果が得られる場合がある。

6

【0014】

【実施例】次に、実施例により本発明を更に具体的に説明する。

実施例1(染料結晶の製造例)

N-ヒドロキシエチルカルバゾール4、2gを10wt%硫酸水溶液200mlにて分散させカップリング成分とした。次に98%硫酸4.6gに43%ニトロシル硫酸6.1gを加え、20～30℃にて攪拌下、2,6-ジクロロ-4-ニトロアニリン4.1gを徐々に添加し、ジアゾ化を行いジアゾ化溶液とした。このジアゾ化溶液を前記カップリング成分溶液中に0～5℃で滴下し、10時間、同温度で攪拌し、析出した結晶を濾別、水洗乾燥して、前示構造式(1)で示される化合物の黄色結晶5.1gを得た。この反応で得られたモノアゾ染料の粉末をX線回折法により分析したところ、図2のX線回折図を示す $\beta$ 型結晶変態であった。

【0015】次いで、得られた $\beta$ 型結晶を、10倍容量の水中に分散させ、90～95℃で3時間攪拌し結晶の転移を行なった。結晶乾燥後濾過、乾燥を行ない、得られた結晶をX線回折法により分析したところ、図1のX線回折図を示す $\alpha$ 型結晶変態であった。

【0016】試験例1(染色例)

前記実施例1で得られた $\alpha$ 型結晶変態のモノアゾ化合物0.2gを、ナフタレンスルホン酸-ホルムアルデヒド縮合物0.2gおよび高級アルコール硫酸エステル0.2gを含む水1リットル中に分散させて染色浴を調製した。

【0017】この染色浴にポリエステル繊維100gを浸漬し、135℃で30分間染色した後、ソービング、水洗および乾燥を行なったところ、染料の分散性は良好であり、染布への均一な染色がなされた。また、得られた染布は黄色で、耐光堅牢度6級、耐摩擦堅牢度5級と良好なものであった。なお、上記製造例の製造途中の $\beta$ 型結晶変態のモノアゾ化合物を用いて、同様の染色試験をしたところ、染浴中で染料の部分凝集が起り、不均染な染布となり、かつ耐摩擦堅牢度は1級と大きく劣るのであった。

【0018】試験例2(染色例)

試験例1において、ナフタレンスルホン酸-ホルムアルデヒド縮合物および高級アルコール硫酸エステルをそれぞれ3倍の0.6gに、水を3倍の3リットルとし、染色条件を130℃で60分間とした以外は試験例1と同様にして、やや温かな染色法にて染色を行なった結果、本発明の $\alpha$ 型結晶変態では、試験例1と同様に良好な染色ができ、得られた染布も耐光堅牢度6級、耐摩擦堅牢度5級と良好であった。これに対して、 $\beta$ 型結晶変態を用いた際には、試験例1に比べて僅かに向上が見られたが、やはり不均染な染布が得られ、耐摩擦堅牢度は3級であった。

【0019】

(4)

特許2506594

7

8

【発明の効果】本発明の特定の結晶変態を有する水不溶性モノアゾ染料は、高温で、しかも、例えば被染物：染色液の比率が1：10、染料ケーキ：分散剤の比率が1：1、染色条件が135℃で0.5時間といった苛酷な染色条件下でも分散安定性が非常に良好であり、得られる染布は耐光堅牢度、耐摩擦堅牢度に優れたものである。従って、本発明の染料は、省資源、省エネルギーの観点から非常に有用なものである。

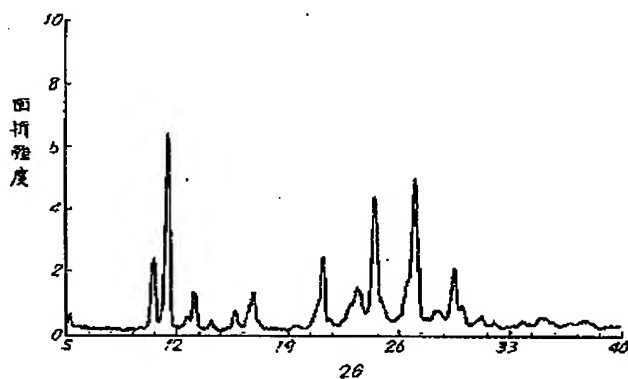
\*

\*【図面の簡単な説明】

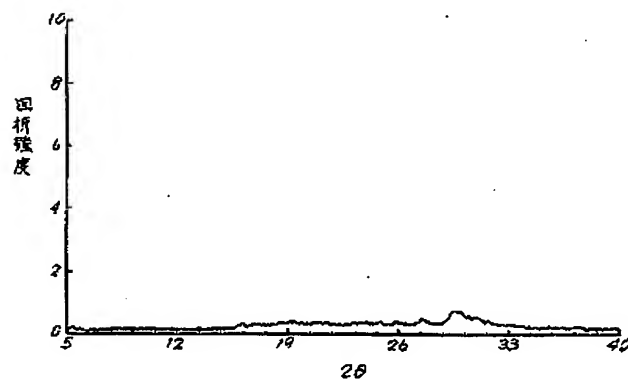
【図1】本発明の実施例において得られたモノアゾ化合物の $\alpha$ 型結晶変態のX線回折図であり、図中、横軸は回折角(2 $\theta$ )を、縦軸は回折強度を表わす。

【図2】本発明の実施例において得られた $\beta$ 型結晶変態のX線回折図であり、図中、横軸は回折角(2 $\theta$ )を、縦軸は回折強度を表わす。

【図1】



【図2】



## \* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

---

DETAILED DESCRIPTION

---

## [Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the yellow system monoazo color which has the new crystal transformation which can dye polyester fiber etc. homogeneity also on severe conditions by the elevated temperature in detail about a monoazo color.

[0002]

[Description of the Prior Art] In recent years, in the dyeing industry, when various rationalization is carried out to the staining technique, for example, it dyes polyester fiber using a disperse dye, as an object for cloth, there is a cheese-dyeing color method or a package staining technique as a liquid flow staining technique and an object for yarn, and it is carried out widely.

[0003] Since these staining techniques are methods which circulate dyeing dispersion liquid compulsorily and make them dye in the precise layer which wound stationary fiber around many layers, it is required more than before that the distributed stability in that the color particle distributed to the dyeing bath is a particle and a dyeing bath should be excellent. If a color particle becomes large, the filtration phenomenon of a color particle will happen by the fiber layer, and problems, such as lowering of fastness, such as antifriction fastness by adhesion of the shade dyeing of the inner layer by poor osmosis of the color inside fiber or adhesion of an aggregate or an outer layer and the color only on the front face of fiber, will occur.

[0004] Therefore, the color used for such a staining technique needs for dispersibility not to fall in a temperature requirement large [ to the high temperature to which actual dyeing takes place from a room temperature good / distribution ] in a dye bath. however, dyeing concentration differs in an outer-layer part and a inner layer part, and, as for the dyed goods-ed which adhered to the front face dyed goods in the shape of filtration residue as the color which boiled the dispersibility of a color occasionally, carried out it, and was easy to fall, consequently was condensed mentioned above, and have generally lapped with many layers when it is made high temperature in a dyeing bath, the dyeing object of uniform concentration is not obtained.

[0005] Especially recently The reduction in the bath ratio of saving resources and the viewpoint of energy saving to \*\* dyeing bath (dyed goods-ed: fall the ratio of a stain solution to 1:10 from 1:30), \*\* Although dyeing conditions are shifting to severe conditions, lowering (color cake: fall the ratio of a dispersant to 1:1 from 1:3) of the operating rate of a dispersant, short-time elevated-temperature-ization with still much more \*\* dyeing conditions (it is 0.5 hours at 135 degrees C from 1 hour in 130 degrees C), etc. No these conditions also have few from which distributed stability becomes poor in the latest severer staining technique also in the color which was the fitness of distributed stability comparatively in the conventional staining technique, in order to work disadvantageously for the distributed stability of a color.

[0006] For example, the monoazo color of a carbazole system shown with a structure expression [I] according to claim 1 is obtained, when the structure itself is well-known and it carries out the coupling reaction of a diazo component and the coupling component according to a conventional method as the process by German JP,2212755,B. In the conventional mild dyeing conditions, this monoazo color can dye polyester fiber homogeneity, and, moreover, many fastness is also excellent. However, it is the above high temperature, and when it dyes under severe conditions, lowering of the dispersibility of a color is remarkable and it is very difficult [ it ] to obtain the dyeing object of

uniform dyeing concentration.

[0007] Moreover, there is a problem also in respect of compatibility with various dyeing assistants, for example, the elevated-temperature distribution stability under salt cake ( $\text{Na}_2\text{SO}_4$ ) existence is remarkable, and this color is bad, therefore in case it uses together with reactive dye etc. and a salt cake carries out the existence bottoming color of polyester / the cotton mix spinning article, it serves as non-level dyeing. Furthermore, also when using it, having blended the color, there was a fault which generates color Bure and non-level dyeing from the point of compatibility with a combination color.

[0008]

[Problem(s) to be Solved by the Invention] This invention offers the color which can perform dyeing good also under conditions severe at high temperature which solved the above-mentioned fault. As a result of this invention persons' examining the above-mentioned fault wholeheartedly, at least two kinds of crystal transformations exist in the monoazo compound of a carbazole system shown with a structure expression [I] according to claim 1, One is the crystal transformation which is not not much good under the dyeing conditions of high temperature as for distributed stability, and the cake obtained at the conventional usual synthetic reaction is this crystal transformation, Moreover, other one found out that distributed stability was a very good new crystal transformation also under severe dyeing conditions by high temperature. Furthermore, when the serious relation not only for the size of a color particle but a crystal transformation was and the compound of the above-mentioned new crystal transformation was used, the stability of the distributed condition in the inside of the elevated-temperature dye bath of a color constituent found out that the distributed stability in the inside of the elevated-temperature dye bath of a color constituent could be attained for the first time, and reached this invention.

[0009]

[Means for Solving the Problem] That is, the summary of this invention makes a summary the water-insoluble nature monoazo color which has the crystal transformation characterized with three strong peaks and X diffraction drawing ( $\text{CuK}\alpha$ ) showing three medium peaks at about 10.3 degrees, 21.1 degrees, and about 29.5 degrees further at about 11.3 degrees (2theta) of angle of diffractions, 24.4 degrees, and about 27.0 degrees and which is shown with a structure expression [I] according to claim 1. The monoazo compound which has the new crystal transformation (henceforth alpha mold crystal transformation) of this invention can be obtained as follows. For example, the monoazo compound of a forecited structure expression [I] is compounded by diazotizing a 2 and 6-dichloro-4-nitroaniline with a conventional method, and subsequently carrying out the coupling reaction of this to N-(hydroxyethyl) carbazole which are 0.5 - 15 hours, and a coupler at the temperature of 0-10 degrees C preferably -5-15 degrees C in a dilute-sulfuric-acid medium. Although the cake of the monoazo compound obtained by this composition is the crystal transformation (henceforth beta mold crystal transformation) almost near a non-fixed form, in this invention, this cake is further considered as alpha mold crystal transformation by processing under specific conditions. As this art, the cake of beta mold crystal transformation is distributed in \*\* water medium, for example. By the case Under existence of dispersants, such as a formaldehyde condensate of a naphthalene sulfonic acid and a concentrate of the sulfite-pulp waste fluid whose ligninsulfonic acid soda is a principal component, At the temperature of 80-100 degrees C, preferably 60-130 degrees C 0.5 - 30 hours, Alcohols, such as the approach of carrying out stirring processing preferably for 1 to 10 hours or \*\* methanol, ethanol, or a butanol, It distributes in organic solvents, such as ether, such as dioxane, ethylene glycol, and glycol ether, and the 15-100 degrees C of the approaches of carrying out stirring processing are preferably adopted at the temperature of 20-80 degrees C for about 0.5 to 10 hours.

[0010] Next, a drawing explains alpha mold crystal transformation of a monoazo compound and beta mold crystal transformation which are shown with a forecited structure expression [I]. Drawing 1 and drawing 2 are X diffraction drawings which recorded the diffraction condition by the  $\text{CuK}\alpha$  rays in a fine-particles X-ray diffraction method using the proportional-spacing counter, an axis of abscissa shows an angle of diffraction (2theta), and an axis of ordinate shows diffraction reinforcement. Drawing 1 shows alpha mold crystal transformation which is the new crystal mold of this invention, and has three medium peaks in about 11.3 degrees (2theta) of angle of diffractions, 24.4 degrees, and about 27.0 degrees especially at three strong peaks and also about 10.3 degrees,

21.1 degrees, and about 29.5 degrees. Drawing 2 shows the conventional beta mold crystal transformation, and differs from alpha mold crystal transformation of drawing 1 clearly.

[0011] If the angle of diffraction by the X-ray diffraction method is the thing of the same crystal mold, it is always a match with an about  $\pm 0.1$ -degree error, and these drawings show the difference of a crystal transformation clearly. The behavior of the monoazo compound at the time of dyeing changes with this crystal type of differences, and in being this invention, it is high temperature, and even if it moreover adopts the staining technique in severe conditions, it can perform good dyeing.

[0012] The mixed elegance of natural fibers, such as polyester fiber which consists of a polycondensation object of polyethylene terephthalate, a terephthalic acid, and a 1 and 4-screw-(hydroxymethyl) cyclohexane etc. as fiber which can be dyed by the monoazo color of the carbazole system of this invention or cotton, and wool, and the above-mentioned polyester fiber, and a mixed fabric article are mentioned. In order to dye polyester fiber using the monoazo color of this invention, the dyeing bath or printing paste distributed in the aqueous medium with the conventional method, using the condensate of a naphthalene sulfonic acid and formaldehyde, a higher-alcohol sulfate, high-class alkylbenzene sulfonates, etc. as a dispersant can be prepared, and dyeing or textile printing can be performed. Moreover, since the monoazo color of this invention is excellent in distributed stability even if it can apply dyeing approaches, such as the above high-temperature-dyeing methods, a carrier dyeing method, and a thermostat sol staining technique, and moreover adopts severe dyeing conditions by these approaches for example, in the case of dyeing, polyester fiber or its mixed elegance can be dyed good. Specifically, the dyeing temperature of 125-140 degrees C and the operating rate of a dispersant of as opposed to 15 or less times and a color in a dye bath ratio are able to carry out uptake dyeing of the polyester fiber under existence of a dispersant among an aqueous medium under the severe conditions not more than 3 weight twice.

[0013] In addition, if acid, such as a formic acid, an acetic acid, a phosphoric acid, and an ammonium sulfate, is added to a dyeing bath by the case, a good result will be obtained further. Moreover, the monoazo color shown with the forecited structure expression [I] used for this invention approach may be used together with other colors, and good results, such as improvement in a dye affinity, may be obtained by combination between colors.

[0014]

[Example] Next, an example explains this invention still more concretely.

Example 1 (example of manufacture of a color crystal)

200ml of 10wt% sulfuric-acid water solutions was made to distribute N-hydroxyethyl carbazole 4.2g at 5-8 degrees C, and it considered as the coupling component. Next, 6.1g of nitrosylsulfuric acids was added to 4.6g of sulfuric acids 43% 98%, and it diazotized by having added gradually 2 and 6-dichloro-4-nitroaniline 4.1g under stirring at 20-30 degrees C, and considered as the diazotation solution. This diazotation solution was dropped at 0-5 degrees C into said coupling component solution, rinsing desiccation of the crystal which stirred and deposited at this temperature was carried out the  $\pm$  exception, and 5.1g of yellow crystals of the compound shown with a forecited structure expression [I] was obtained for 10 hours. When the powder of the monoazo color obtained at this reaction was analyzed with the X-ray diffraction method, it was beta mold crystal transformation which shows X diffraction drawing of drawing 2.

[0015] Subsequently, underwater [ of capacity ] was distributed 10 times, obtained beta mold crystal was stirred at 90-95 degrees C for 3 hours, and the crystal was transferred. When after [ crystal transition ] filtration and desiccation were performed and the obtained crystal was analyzed with the X-ray diffraction method, it was alpha mold crystal transformation which shows X diffraction drawing of drawing 1.

[0016] The example 1 (example of dyeing) of a trial

0.2g of monoazo compounds of alpha mold crystal transformation obtained in said example 1 was distributed in 1l. of water containing 0.2g of naphthalene sulfonic-acid-formaldehyde condensates, and 0.2g of higher-alcohol sulfates, and the dyeing bath was prepared.

[0017] After being immersed in this dyeing bath and dyeing 100g of polyester fiber it for 30 minutes at 135 degrees C, when soaping, rinsing, and desiccation were performed, the dispersibility of a color is good and uniform dyeing to a colored cloth was made. Moreover, the obtained colored cloth was yellow and as good as the 6th class of color fastness to light, and the 5th class of antifriction

fastness. In addition, when the same dyeing test was carried out using the monoazo compound of beta mold crystal transformation in the middle of manufacture of the above-mentioned example of manufacture, partial condensation of a color took place in the dye bath, it became an un-level dyeing colored cloth, and antifriction fastness was the 1st class and a thing which is greatly inferior.

[0018] The example 2 (example of dyeing) of a trial

In the example 1 of a trial a naphthalene sulfonic-acid-formaldehyde condensate and a higher-alcohol sulfate, respectively to 3 times as many 0.6g as this As well as the example 1 of a trial as a result of dyeing in a little mild staining technique, except having made water into 3 times as many 3l. as this, and having set dyeing conditions as for 60 minutes at 130 degrees C in alpha mold crystal transformation of this invention Good dyeing was completed like the example 1 of a trial, and the obtained colored cloth was also as good as the 6th class of color fastness to light, and the 5th class of antifriction fastness. On the other hand, although improvement was slightly found compared with the example 1 of a trial when beta mold crystal transformation was used, the un-level dyeing too colored cloth was obtained, and the number of antifriction fastness was three. .

[0019]

[Effect of the Invention] the water-insoluble nature monoazo color which has the specific crystal transformation of this invention -- high temperature -- it is -- moreover -- for example, -- -ed -- also under the severe dyeing conditions of 0.5 hours in 1:1 and dyeing conditions, distributed stability is dramatically good and the colored cloth obtained excels [ the ratio of 1:10 and a color cake:dispersant / degrees C / 135 ] in the ratio of a dyed-goods:stain solution at color fastness to light and antifriction fastness. Therefore, the color of this invention is very useful from saving resources and a viewpoint of energy saving.

---

[Translation done.]



## \* NOTICES \*

JPO and NCIPi are not responsible for any damages caused by the use of this translation.

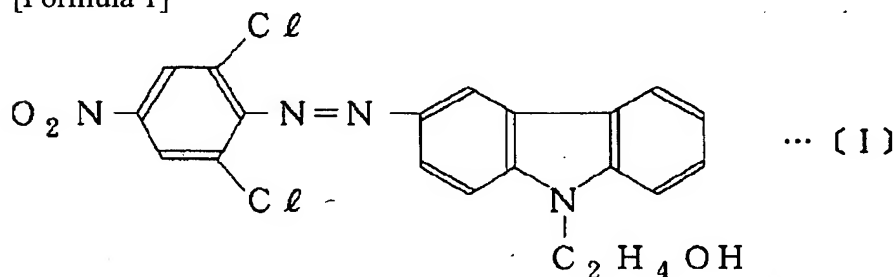
1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. \*\*\*\* shows the word which can not be translated.
3. In the drawings, any words are not translated.

## CLAIMS

(57) [Claim(s)]

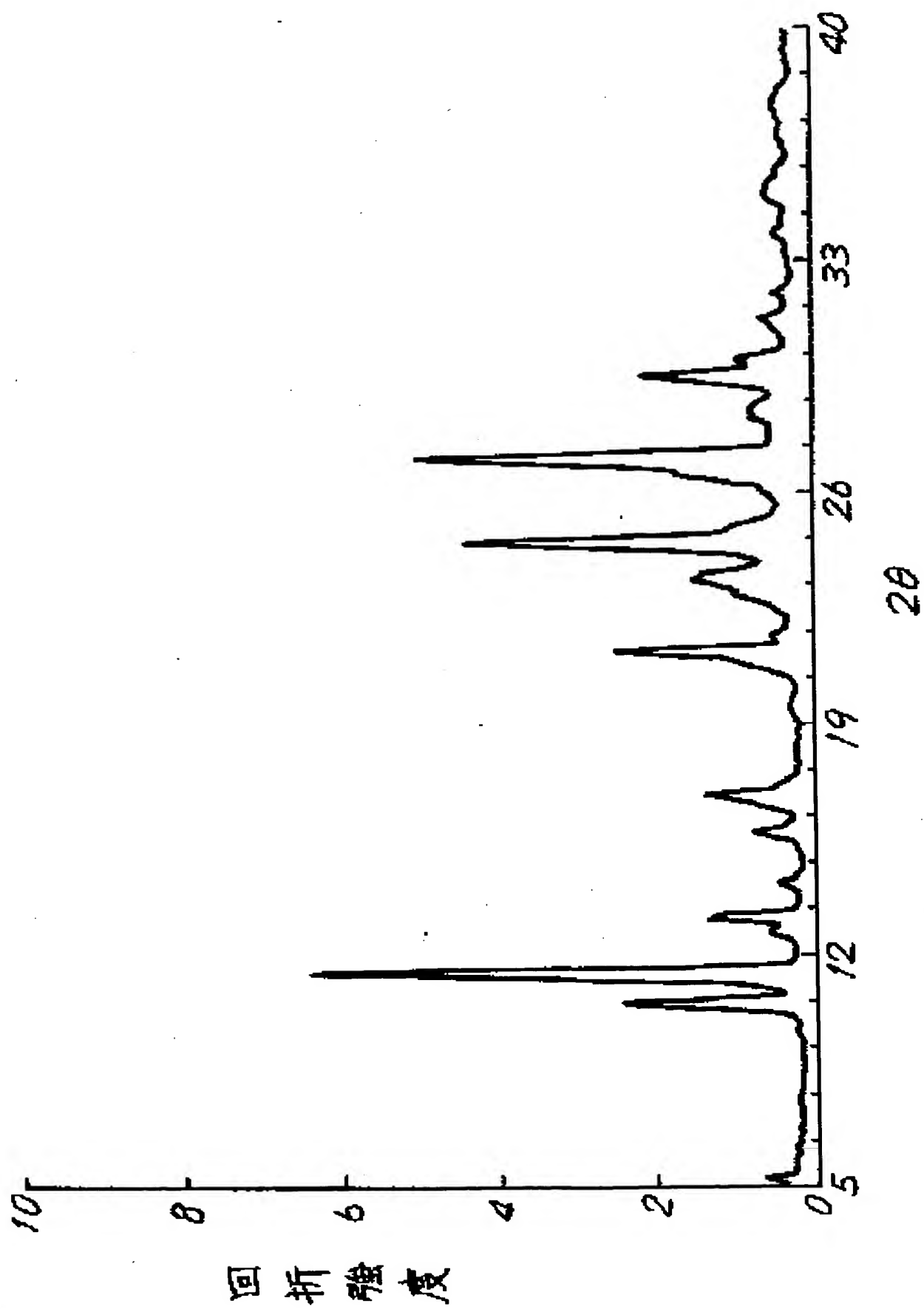
[Claim 1] The following structure expression which has the crystal transformation characterized with three strong peaks and X diffraction drawing (CuKalpha) showing three medium peaks at about 10.3 degrees, 21.1 degrees, and about 29.5 degrees further at about 11.3 degrees (2theta) of angle of diffractions, 24.4 degrees, and about 27.0 degrees [I]

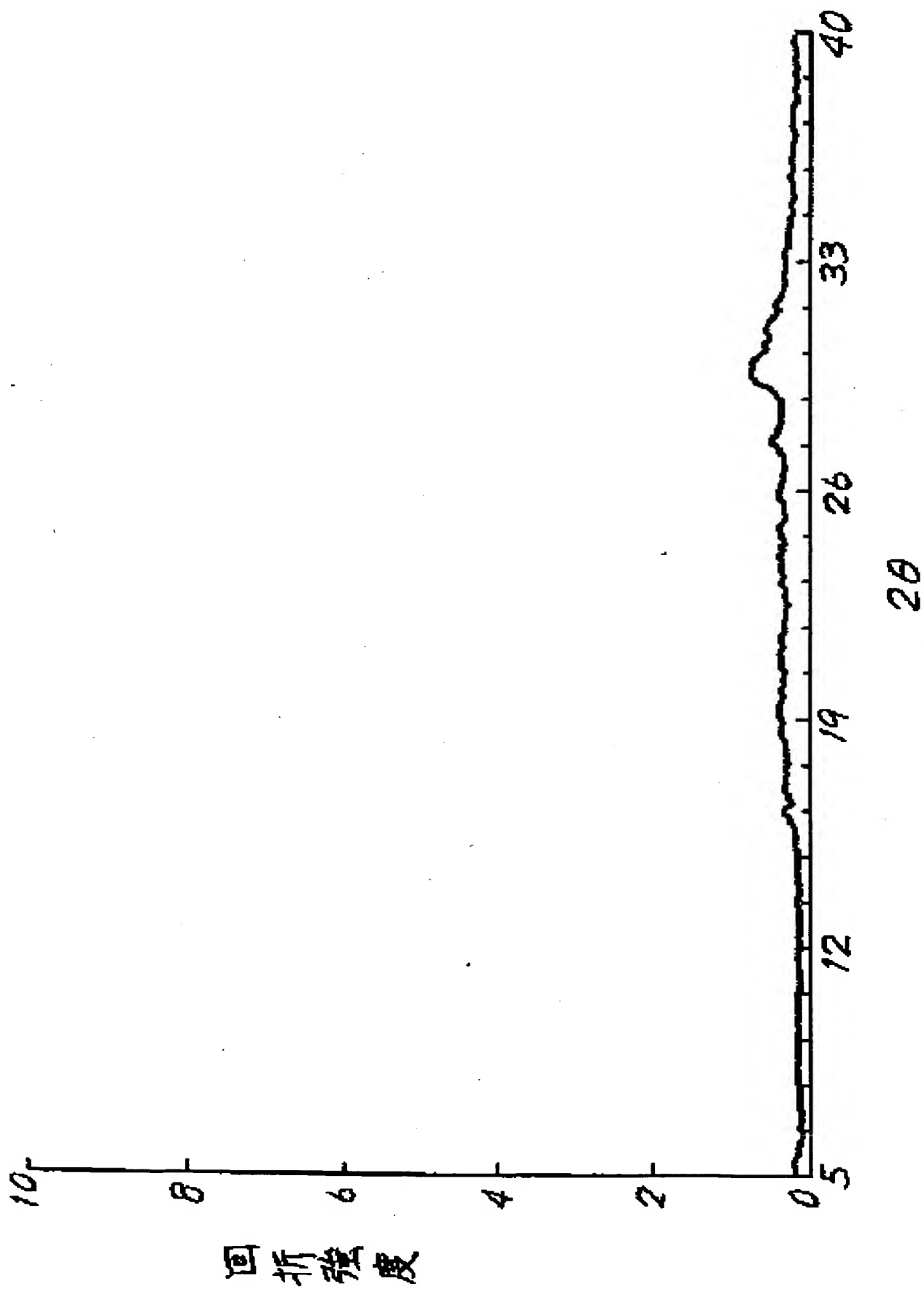
[Formula 1]



The water-insoluble nature monoazo color come out of and shown.

[Translation done.]





Drawing 2

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☐ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**